

## Studies on the Fuel Electrodes of Liquid Fuel Cells

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### (1) Introduction

Various activation catalyst metals have been used as the electrodes of alkaline liquid fuel cell (1), (2), (3). However, some ambiguity exists as to what the properties of such activation catalyst metals are and in what state and to what liquid fuels these electrodes are actually suited.

The present authors have used typical alkali-resistant metals, i.e. Au, Ag, Pt, Pd, Ni and Cu as catalyst metals, and formaldehyde (4), hydrazine (5), (6) and methanol, which are conventional and typical fuels as liquid fuels in consideration of reaction velocities (7). They have examined various combinations of these liquid fuels with the above-mentioned catalyst metals and studied the resulting polarization characteristics.

In the experiment performed, the electrodes prepared by forming various catalyst metal powders under the pressure of 2 tons/cm<sup>2</sup> were immersed in a mixture of each of the fuels tested and an alkaline electrolyte, and the resulting polarization characteristics were measured.

The results have shown that Pt, Pd and Au powders which have high oxygen over-potentials and low hydrogen potentials are preferred. Then, the authors have prepared such powders having different surface areas, and studied the resulting polarization characteristics.

Lastly, with the electrodes prepared by forming the activation catalyst powders of Pt and Pd having the surface areas of 32.9 m<sup>2</sup>/gr. and 31.8 m<sup>2</sup>/gr., respectively, polarization characteristics were measured in mixtures of the alkaline electrolyte and various mono, di, tri and polyhydric saturated alcohols having different numbers of carbon atoms to find the manner in which the activation catalysts would act upon the different fuel alcohols.

### (2) Experiment

#### (2.1) Preparation of Metal Powders

The following metal powders were used:

- a) Copper Powder; purity 99.97%, electrolysis.
- b) Iron Powder; purity 99.992%, carbonyl iron powder (Mond Chemical).
- c) Nickel Powder; purity 99.998%, carbonyl nickel powder (Mond Chemical B type).
- d) Silver Powder; purity 99.97%, by dissolving 10 gr. AgNO<sub>3</sub> in 10 cc. pure water, adding 50 cc. HCHO and 85 cc. 50% KOH while cooling, allowing to stand for 2 hours, washing and drying.

- e) Palladium Black; purity 99.98%, by dissolving 10 gr.  $\text{PdCl}_2$  in 20 cc. 5%  $\text{HCl}$ , adding 50 cc. 30%  $\text{HCHO}$  and 87 cc. 50%  $\text{KOH}$  while cooling, allowing to stand for 2 hours, washing and drying.
- f) Gold Black; purity 99.96%, by dissolving 10 gr.  $\text{HAuCl}_4$  in 200 cc. pure water, adding 55 cc. 33%  $\text{HCHO}$  and 92 cc. 50%  $\text{KOH}$  while cooling, allowing to stand for 2 hours, washing and drying.
- g) Platinum Black; purity 99.975%, by dissolving 10 gr.  $\text{H}_2\text{PtCl}_6$  in 200 cc. pure water, adding 60 cc. 33%  $\text{HCHO}$  and 98 cc. 50%  $\text{KOH}$ , allowing to stand for 2 hours, washing and drying.
- h) Heat-treated Powders; each of the above blacks was heat-treated in nitrogen gas at  $200^\circ$ ,  $400^\circ$  and  $600^\circ\text{C}$ . for 20 minutes.
- i) Thermodecomposed Powders; purity Pd 99.98%, Pt 99.995%, Au 99.96%, heating  $\text{H}_2\text{PtCl}_6$ ,  $\text{PdCl}_2$ , and  $\text{HAuCl}_4$ , respectively, at  $500^\circ\text{C}$ . in an electric furnace, followed by thermodecomposition in nitrogen gas for 20 minutes.

## 2.2) Preparation of Activation Catalyst Metal Electrodes

Each of the test electrodes was prepared by weighing 300 mg. of metal powder and forming it under the pressure of 2 tons/cm<sup>2</sup> into a disc, about 15 mm. in diameter and about 0.5 mm in thickness.

## 2.3) Method of Measurement

### a) Measurement of Surface Areas

In order to ascertain the relationship between the surface areas and electrode characteristics of the various metal powders prepared in (2.1) (i.e. the black, the heat-treated and the thermodecomposed samples), the surface area of each test electrode was measured by B.E.T. method.

### b) Measurement of Polarization Characteristics with Various Fuel Electrodes.

Each of the test electrodes prepared as per (2.2) was immersed in a mixed solution containing 10 parts of 25% aqueous solution of  $\text{KOH}$  and 2 parts of each fuel and the polarization characteristics on anodic oxidation were measured with an opposite electrode of Ni plate. With a reference electrode of  $\text{Hg/HgO}$  1N- $\text{KOH}$ , polarization characteristics at various current densities were measured at  $20^\circ\text{C}$ . Fig. 1 shows the experimental arrangement used.

## (3) Results of Measurements

### (3.1) Measurement of the Surface Areas of Various Metal Powders

The results are given in Table 1.

Organically reduced powders are generally known as metallic blacks and have comparatively large surface areas. Reductions in surface area due to heat-treatment are linearly distributed. The samples prepared by thermodecomposition of metallic salts show

smaller surface areas at the same temperature of heat treatment.

### (3.2) Polarization Characteristics with Various Activation Catalyst Metals

For the purpose of ascertaining the properties of various activation catalyst powders, i.e. Pt, Pd, Au, Ag, Ni and Cu, the powder surface area of 0.18 to 0.75 m<sup>2</sup>/gr. was selected so that the influences due to variety in surface area might be minimal.

#### a) Formaldehyde

With various electrodes prepared as per (2.2), polarization characteristics were measured in a mixture of 10 parts 25% KOH and 2 parts formaldehyde at current densities of 0-100 ma/cm<sup>2</sup>. The results are shown in Fig. 2. The order of increasing polarization is Au, Pt, Pd, Ag, Ni and Cu.

#### b) Hydrazine

Polarization characteristics were measured in the same manner as above by immersing each metal powder electrode in a mixture of 10 parts 25% KOH and 2 parts hydrazine. The results have shown that Ni, Pt and Pd powders exhibits superior characteristics. (See Fig. 3).

#### c) Methanol

In a mixture of 10 parts 25% KOH and 2 parts methanol, polarization characteristics were measured in the same manner as above. It will be apparent from Fig. 4 that Pt, Pd and Au are superior in that order. The other metals showed quite unsatisfactory results.

### (3.3) Polarization Characteristics by Surface Area with Pt, Pd and Au Electrodes

#### a) Formaldehyde

The Pt, Pd and Au blacks prepared as per (2.1), each having a various surface area, were used as electrodes and polarization characteristics were measured with respect to formaldehyde. Fig. 5 shows the relationship between the polarization potentials of the Pt, Pd and Au electrodes on anodic oxidation at the current density of 500 ma/cm<sup>2</sup> and the surface areas of those activation catalyst metal powders.

For all of Pt, Pd and Au, the difference in surface area of the electrode does not exert any great influence. If the electrode is made of a powder which surface area is about 1.0 m<sup>2</sup>/gr., there will be a relatively low degree of polarization on anodic oxidation even at 500 ma/cm<sup>2</sup> and invariably satisfactory results are obtained with any of the above-mentioned catalyst metals.

b) Hydrazine

The Pt, Pd and Au blacks prepared as per (2.1), each having a various surface area, were used as electrodes and polarization characteristics were measured with respect to hydrazine in the same manner as (2.2). Fig. 6 shows the relationship between the polarization potential of the electrodes on anodic oxidation at 200 ma/cm<sup>2</sup> in hydrazine and the surface areas of the electrode metals. In the case of Pt, there was no significant difference in characteristics due to changes in surface area, just as it was the case with formaldehyde. However, with the Pd electrodes, there was found a slightly significant influence, for the electrode potential was altered more appreciably within the range of 8.54 m<sup>2</sup>/gr. - 1.67 m<sup>2</sup>/gr. than within the range of more than 8.54 m<sup>2</sup>/gr. Moreover, with respect to Au, the influence of smaller surface areas was conspicuous and when it was less than 1.0 m<sup>2</sup>/gr., the degree of polarization was inordinately high.

c) Methanol

The Pt, Pd and Au blacks prepared as per (2.1), each having a various surface area, were used as electrodes and polarization characteristics were measured with respect to methanol in the same manner as (2.2). Fig. 7 shows the relationship between the electrode potential in methanol on anodic oxidation at the current density of 100 ma/cm<sup>2</sup> and surface areas of those catalyst metal powders.

Compared with formaldehyde and hydrazine, the influences of differences in surface area were conspicuous for all the Pt, Pd and Au electrodes. Among them, the influences were relatively minor in the case of Pt, while a slightly higher degree of polarization was observed in the case of Pd. With respect to the Au electrodes, which generally have smaller surface areas, considerably high degrees of polarization were observed on anodic oxidation at 100 ma/cm<sup>2</sup>. Within the range of surface areas which could be measured, there was a greater influence of changes in surface area of Au powders than in the case of Pt and Pd.

(3.4) Polarization Characteristics with Various Electrodes in Saturated Alcohols

Polarization characteristics were measured with Pt and Pd black electrodes in various saturated alcohols and their isomers.

a) Pt Electrode Characteristics by the C-number of Mono, Di and Tri, and their isomers.

- (1) With the Pt black electrodes prepared as per (2.1) and (2.2), polarization characteristics on anodic oxidation were measured to ascertain the influences of the C-numbers of mono, di and trihydric alcohols and the isomers of monohydric alcohol. Fig. 8 shows the characteristics obtained with monohydric alcohols having different C-numbers and their isomers. In Fig. 9 are shown the polarization characteristics with dihydric alcohols having different C-numbers. Fig. 10 shows the influences of trihydric alcohols

As regards monohydric alcohols, the C-number range surveyed was from  $C_1$  to  $C_{10}$ ; dihydric alcohols from  $C_2$  to  $C_{10}$ ; trihydric alcohols from  $C_3$  to  $C_5$ . According to Fig. 8, it is found that the greater the C-number is, the higher the degree of polarization is. As regards their isomers, the degree of polarization increases in the order of iso, sec and tert, and extremely high degrees of polarization are obtained with propyl and higher alcohols. With regard to di and trihydric alcohols (See Fig. 9 and 10.), the degree of polarization increases in C-numbers as it is the case with monohydric alcohols. In the case of dihydric alcohols, high degrees of polarization are obtained with  $C_5$  and up. In regard to trihydric alcohols, the degree of polarization is relatively low up to  $C_5$ .

- (ii) Pt Electrode Characteristics with Various Saturated Alcohols, Each Containing the Same Number of C and OH.

With the same Pt black electrode as (a-i), polarization characteristics were measured for mono to hexahydric alcohols, each containing the same number of C and OH. It will be apparent from Fig. 11 that the degree of polarization increases in the order of mono, di and trihydric alcohols, but that in the case of polyhydric alcohols, even hexahydric alcohols shows a relatively low degree of polarization.

- b) Pd Electrode Characteristics by the C-number of Mono, Di Tri and Polyhydric Alcohols and their Isomers.

- 1) With the Pd black electrodes prepared as per (2.1) and (2.2), polarization characteristics on anodic oxidation were measured to ascertain the influences of the numbers of C atoms contained in mono, di and trihydric alcohols. Fig. 12 shows the influences of the C-numbers of monohydric alcohols and their isomers. Similar influences for dihydric alcohols are illustrated in Fig. 13 and Fig. 14 relates to trihydric alcohols. It will be apparent from Fig. 12, 13 and 14 that just as with the Pt black electrode mentioned-above, the greater the C-number is, the higher the degree of polarization is, and that as regards the various isomers, the degree of polarization is higher in the order of iso, sec and tert.

The degree of polarization is pronounced with propyl and higher alcohols. In the case of dihydric alcohols, the degree of polarization is conspicuously high for  $C_5$  and up, while trihydric alcohols show relatively low degrees of polarization up to  $C_5$ , just as it is the case with the Pt black electrode.

- ii) Pd Electrode Characteristics for Various Alcohols, Each Containing the Same Number of C and OH.

With the same Pd black electrodes as (b-i), polarization characteristics were measured for mono to hexahydric alcohols, each having the same number of C and OH. (See Fig. 15) The degree of

polarization is higher in the order of  $\text{CH}_3\text{OH}$ ,  $\text{C}_2\text{H}_4(\text{OH})_2$ ,  $\text{C}_3\text{H}_5(\text{OH})_3$  and so on, although it is still relatively low even in the case of hexite.

#### (4) Discussion

In order to ascertain the characteristics of various activation catalyst metals as electrodes, we have selected certain metals on the basis of their chemical reactivities in mixtures of an alkaline solution and various liquid fuels, and studied the polarization characteristics of the above activation catalysts for different fuels. The fuels used are those which are readily miscible with electrolyte KOH. Thus, we have used formaldehyde which is capable of undergoing Cannizzaro's reaction, hydrazine which is partially decomposed in the presence of catalysts, and methanol which is only sparingly decomposed in the presence of the catalysts. Considering the characteristics of various electrode metals with respect to formaldehyde, as will be apparent from Fig. 2, any of the metals tested is useful. However, the order of preference is Au, Pt, Pd, Ag, Ni and Cu, and it is found that even if a metal having somewhat high hydrogen over-potential, e.g. Ag, is employed a satisfactory result may still be obtained so long as it also has a sufficiently high oxygen over-potential. In other words, a high oxygen over-potential is a primary requirement.

It will be seen from Fig. 5 that since only minor differences in characteristics are attributable to differences in surface area of catalyst metal, the only requirement for the electrode is that it should be an effective current collector. From the polarization characteristics for hydrazine, it is found that whereas only unsatisfactory results are obtained with Ag which exhibits relatively good characteristics with formaldehyde (Fig. 3), considerably better results are obtained with Ni. It is presumed, therefore, that in addition to a high oxygen over-potential, a low hydrogen over-potential is essential. Furthermore, in view of the catalytic decomposition of hydrazine, it is thought that sufficiently satisfactory polarization characteristics are obtained when the surface area of the catalyst metal powder is larger than  $1.0 \text{ m}^2/\text{gr}$ . (See Fig. 6)

With regard to methanol, it will be apparent from Fig. 4 that better results are obtained in the order of Pt, Pd and Au, while the other metals are quite unsatisfactory in respect of polarization characteristics. Thus, in addition to the above-mentioned requirement of high oxygen over-potential and low hydrogen over-potential, it is found that, as will be seen from Fig. 7, the greater the surface area of the activation catalyst metal is, whether it is Pt or Pd, the more satisfactory the polarization characteristics are. At least, within the range of measurement described above, a logarithmically linear relation holds between polarization potential and the surface area of the activation catalyst metal. It will also be seen that to activate methanol, a surface area of more than about  $20 \text{ m}^2/\text{gr}$ . is required. Thus, by selecting a large surface area, the catalytic oxidation may be accelerated.

Then, with the so-called metal black electrodes of Pt and Pd powders having maximal surface areas, we have studied the influences

on polarization characteristics of the number of C atoms in various mono, di, tri and polyhydric alcohols. Pt and Pd exhibit the same tendency, and the degree of polarization increases in higher alcohols of each group. As regards their isomers, the degree of polarization is higher in the order of n, iso (8), sec and tert. On the other hand, even when the C-number is large, polyhydric alcohols, which contain many OH groups, shows only low degrees of polarization and therefore, can serve as effective fuels. Especially satisfactory results are obtained when given alcohol contains the same number of C atoms and OH groups, e.g. in the case of methanol, ethylene glycol, glycerin, erythrite, adonite and mannite. (See Fig. 11 and 15.) It is presumed, therefore, that when the activation catalysts of Pt and Pd are used as electrodes, the OH groups have an important role on the anodic oxidation of alcohols, improving their polarization characteristics. With respect to hydrocarbons, it is presumably difficult to be activated even if the surface area of Pt or Pd is made extremely large. Thus, it is preferable to employ alcohols whose numbers of C atoms and OH groups are the same or not substantially different. If Pt and Pd black electrodes are used as activation catalysts, polyhydric alcohols having substantially the same number of C atoms and OH groups will prove to be effective fuels for a liquid fuel cell.

#### (5) Acknowledgement

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#### (6) References

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Table 1.-SURFACE AREA OF VARIOUS METAL POWDERS

con- dition kinds of metal	Powder red- uced by formaldehyde (m <sup>2</sup> /g)	Powder by heat treating metal black			direct thermo decomposi- on of metall- ic salts (m <sup>2</sup> /g)
		200°C 20 <sup>min</sup> (m <sup>2</sup> /g)	400°C 20 <sup>min</sup> (m <sup>2</sup> /g)	600°C 20 <sup>min</sup> (m <sup>2</sup> /g)	
Pt	32.9	15.54	8.18	2.74	0.18
Pd	31.8	20.7	8.54	1.67	0.20
Au	3.55	2.56	1.345	0.735	0.02
Ag	0.19				

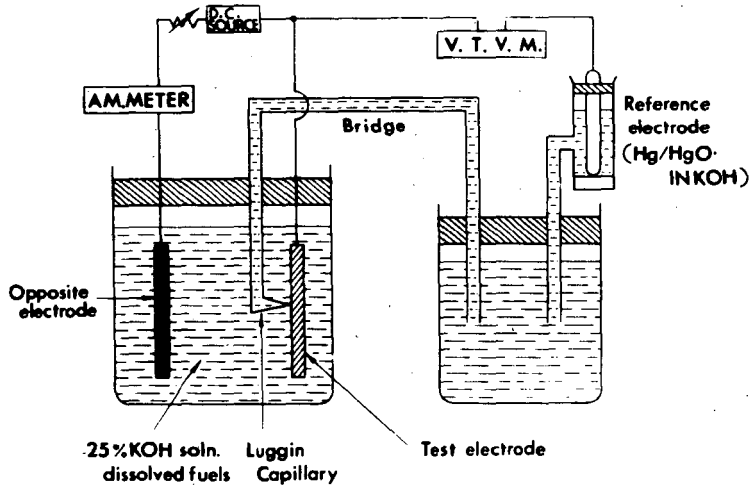


Fig. 1.-EXPERIMENTAL ARRANGEMENT FOR MEASUREMENT OF ANODIC POTENTIALS



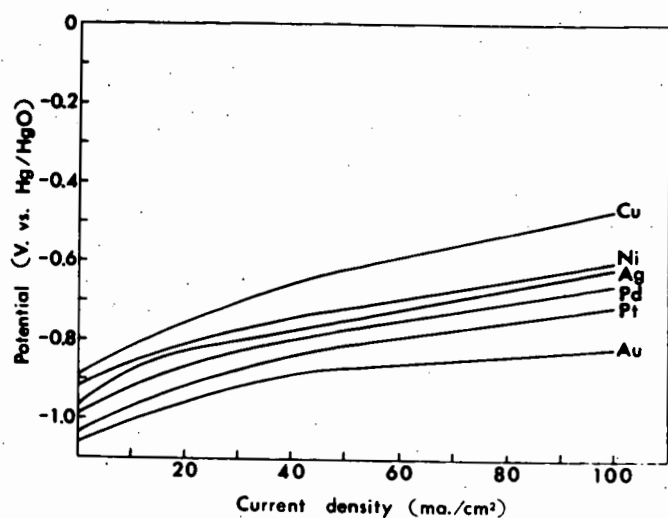


Fig. 2.-ANODIC OXIDATION POTENTIALS OF VARIOUS ACTIVATION CATALYST METALS IN FORMALDEHYDE

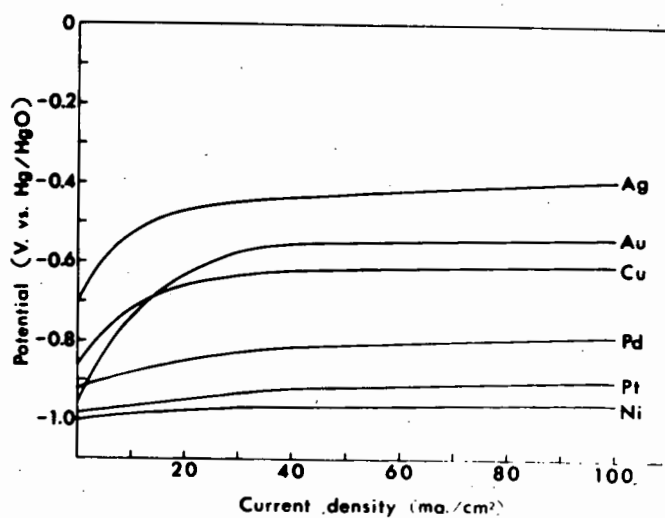


Fig. 3.-ANODIC OXIDATION POTENTIALS OF VARIOUS ACTIVATION CATALYST METALS IN HYDRAZINE

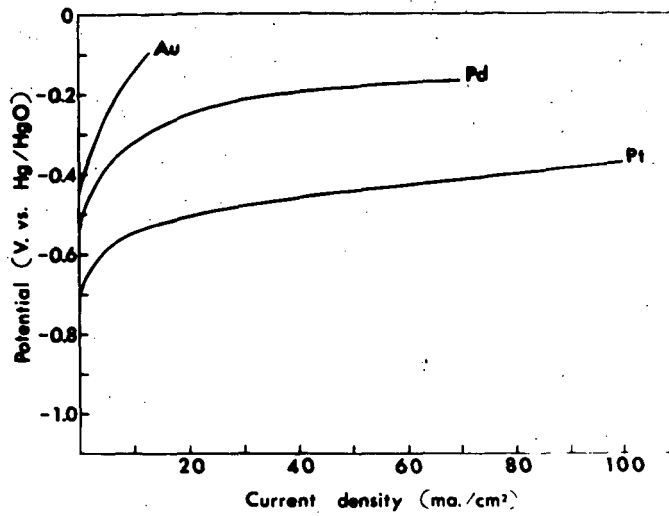


Fig. 4.-ANODIC OXIDATION POTENTIALS OF VARIOUS ACTIVATION CATALYST METALS IN METHANOL

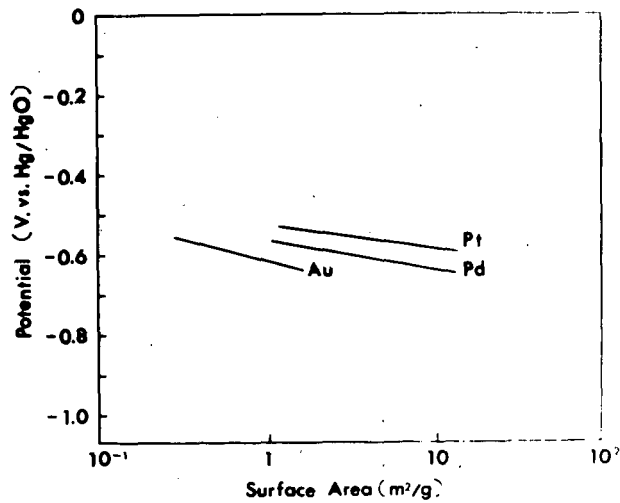


Fig. 5.-ANODIC OXIDATION POTENTIALS vs SURFACE AREA OF Pt, Pd, AND Au IN FORMALDEHYDE AT CURRENT DENSITY OF 500 MA/CM<sup>2</sup>

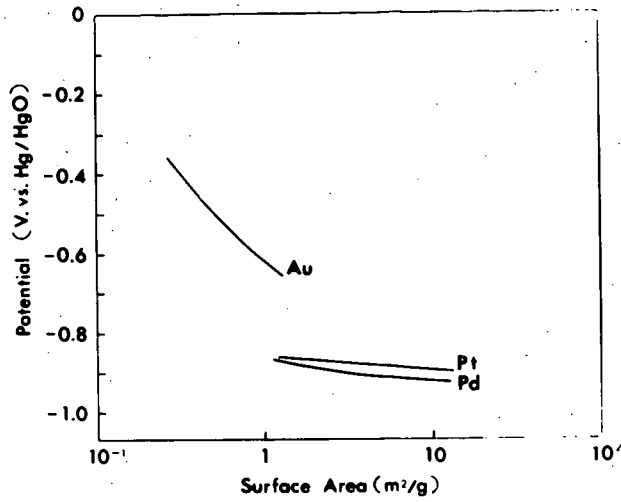


Fig. 6.-ANODIC OXIDATION POTENTIALS vs SURFACE AREA OF Pt, Pd, AND Au IN HYDRAZINE AT CURRENT DENSITY OF 200 MA/CM²

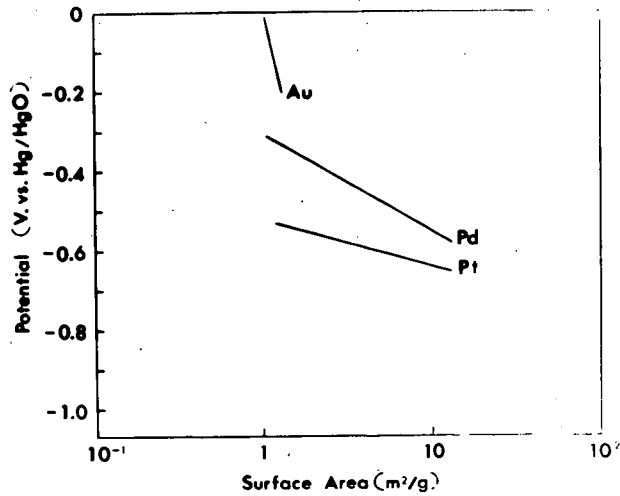


Fig. 7.-ANODIC OXIDATION POTENTIALS vs SURFACE AREA OF Pt, Pd, AND Au IN METHANOL AT CURRENT DENSITY OF 100 MA/CM²

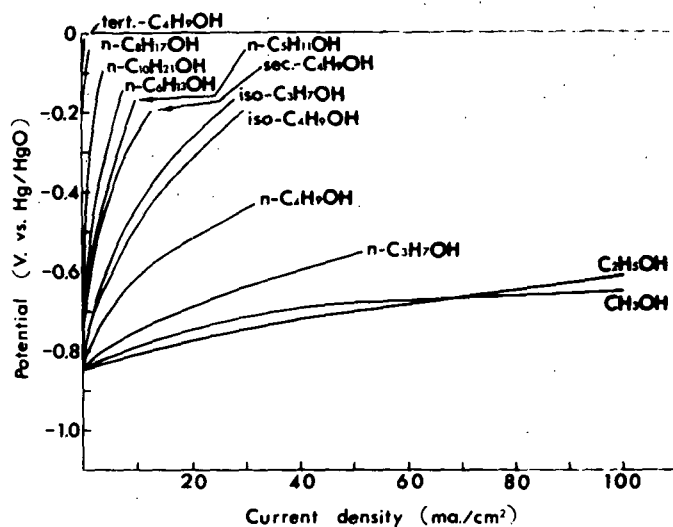


Fig. 8.-Pt ANODIC POTENTIALS WITH THE C-NUMBER AND THEIR ISOMERS OF MONOHYDRIC ALCOHOLS

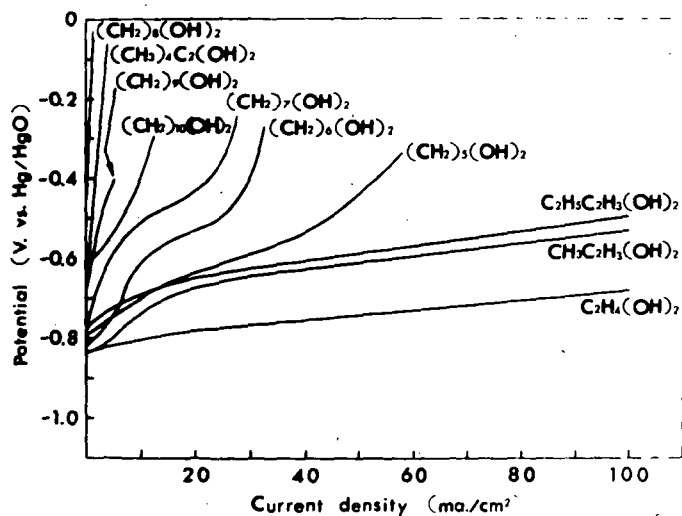


Fig. 9.-Pt ANODIC POTENTIALS WITH THE C-NUMBER OF DIHYDRIC ALCOHOLS

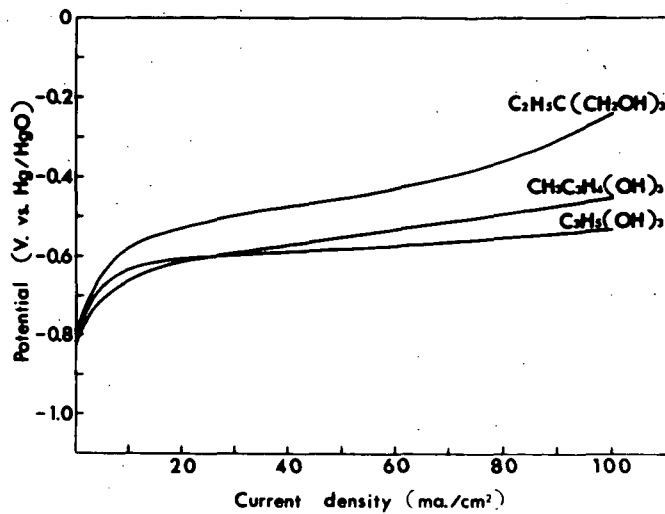


Fig. 10.-Pt ANODIC POTENTIALS WITH THE C-NUMBER OF TRIHYDRIC ALCOHOLS

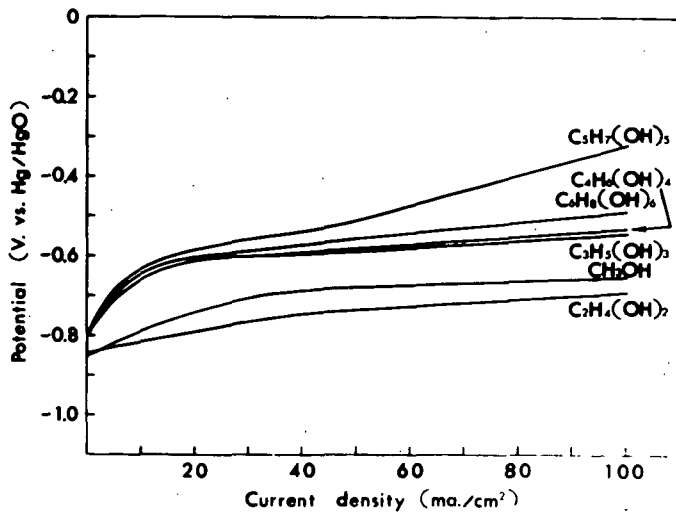


Fig. 11.-Pt ANODIC POTENTIALS WITH VARIOUS ALCOHOLS EACH CONTAINING THE SAME NUMBER OF C AND OH

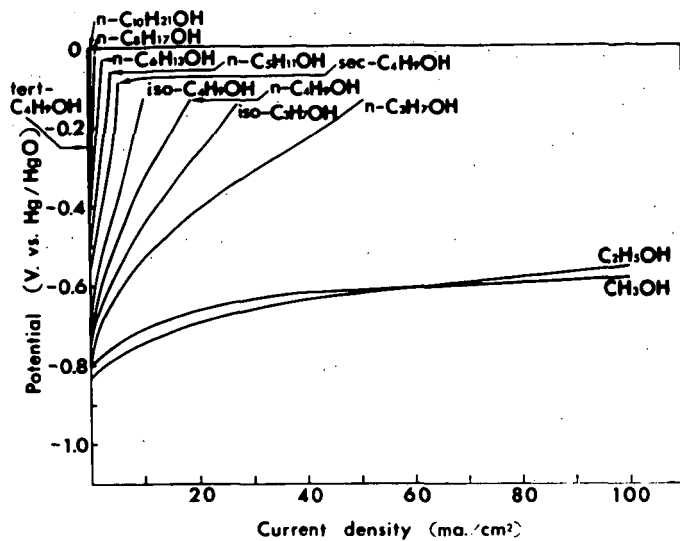


Fig. 12.-Pd ANODIC POTENTIALS WITH THE C-NUMBER AND THEIR ISOMERS OF MONOHYDRIC ALCOHOLS

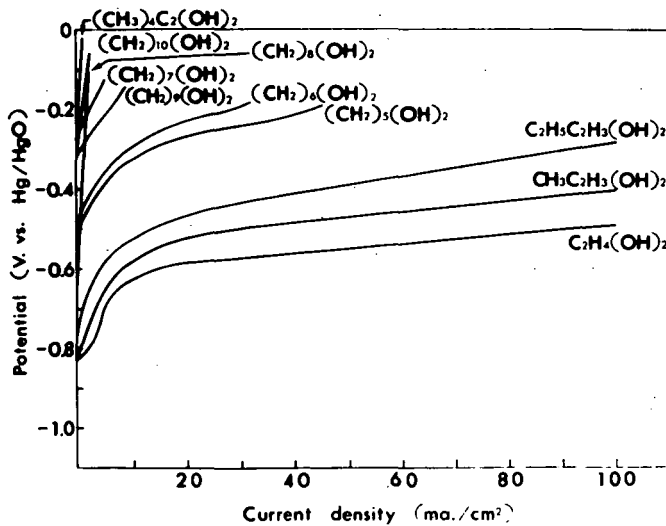


Fig. 13.-Pd ANODIC POTENTIALS WITH THE C-NUMBER OF DIHYDRIC ALCOHOLS

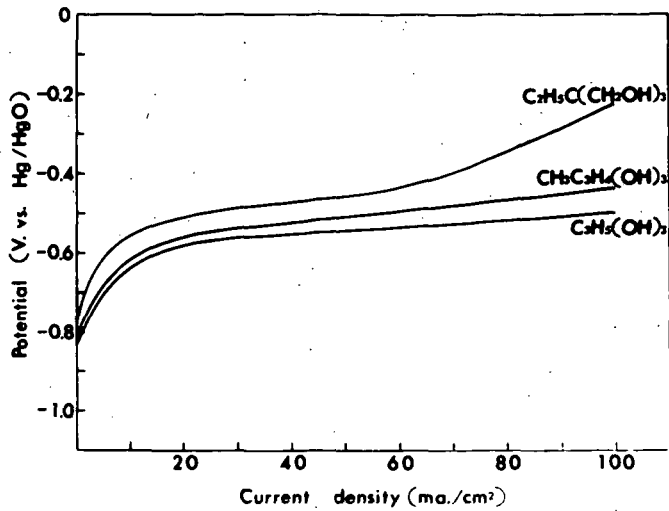


Fig. 14.-Pd ANODIC POTENTIALS WITH THE C-NUMBER OF TRIHYDRIC ALCOHOLS

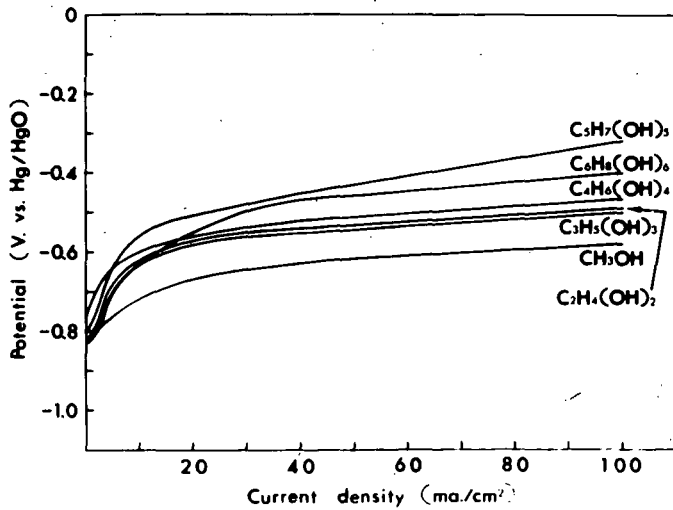


Fig. 15.-Pd ANODIC POTENTIALS WITH VARIOUS ALCOHOLS EACH CONTAINING THE SAME NUMBER OF C AND OH